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(21)Application number : 2000-015369 (71)Applicant : HITACHI METALS LTD

(22)Date of filing : 25.01.2000 (72)Inventor : TANIGUCHI FUMITAKE

## (54) R-T-B PERMANENT MAGNET

### (57)Abstract:

PROBLEM TO BE SOLVED: To provide an R-T-B permanent magnet, that is superior in corrosion resistance and where the heat resistance of magnetic characteristics is improved by reducing the quantity of hydrogen contained within plating in the plated R-T-B permanent magnet is set to 100 ppm or lower.

SOLUTION: The R-T-B permanent magnet whose surface is coated with the plating, where an R2T14B base intermetallic compound (R is one kind, or two kinds or more of rare earth elements which include Y, and T is Fe or Fe and Co) is a main phase, characterized in that the content of hydrogen of the plating is set equal to 100 ppm or lower.

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CLAIMS

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[Claim(s)]

[Claim 1] R-T which makes the main phase an R2T14B mold intermetallic compound (R is one sort of the rare earth elements containing Y, or two sorts or more, and T is Fe, or Fe and Co) R-T-B system permanent magnet which is a R-T-B system permanent magnet which comes to cover plating to - system permanent magnet body surface, and is characterized by setting the hydrogen content of said plating to 100 ppm or less.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the R-T-B system permanent magnet which comes to cover the plating used for a rotating machine (a motor, generator), an actuator, a loudspeaker, or a pump.

[0002]

[Description of the Prior Art] The R-T-B system sintered magnet (R is one sort of the rare earth elements containing Y or two sorts or more, and T is Fe, or Fe and Co) which makes the main phase an R<sub>2</sub>T<sub>14</sub>B mold intermetallic compound among rare earth permanent magnets has high magnetic properties, and since it excels in a ferrite magnet subsequently to cost performance, the amount of manufactures has been extended greatly in recent years. However, it has the fault of being easy to corrode since rare earth elements and iron are contained so much as the major component, and various surface treatment for improving corrosion resistance is performed, and practical use is presented. As surface-preparation film, although resin coating, the clo mate film, or plating is adopted, the method of galvanizing the metallic film represented by especially nickel plating is excellent in corrosion resistance, abrasion resistance, etc., and is used abundantly. Although the R-T-B system permanent magnet which covered plating is used being included in various magnet application products, the needs of a heat-resistant specification have been increasing in recent years. The conventional R-T-B system permanent magnet which covered plating has the problem that the thermal resistance of magnetic properties is bad. That is, the R-T-B system permanent magnet which the former galvanized has the problem that the percentage reduction of the amount of total magnetic flux at the time of heating becomes large notably compared with a non-galvanized thing. For example, when the heat test continuously returned to a rectangular plate-like R-Fe-B system permanent magnet object with a 3mm[ 5mm by ] x thickness of about 0.7mm to an after [ predetermined time maintenance ] room temperature at 70 degrees C in atmospheric air after producing what covered nickel plating (permeance coefficient Pc=0.42) is performed so that it may mention later, the percentage reduction of the amount of total magnetic flux is so large that it reaches to 10%. Thus, remarkable degradation of the magnetic properties at the time of heating of the galvanized conventional R-T-B system permanent magnet was a serious problem.

[0003] Next, plating is explained. The method of galvanizing a metallic film is roughly divided into electroplating and nonelectrolytic plating. the same metal as the metal which you are going to use [ metal ] the galvanized body as cathode and is going to make it electrodeposit it in the electrolytic solution which contains in electroplating the metal ion which it is going to galvanize -- or if direct-current electrolysis is performed by making an insoluble metal into an anode plate, the metal ion which you are going to make it electrodeposit in cathode can discharge, and a galvanized body surface can be made to electrodeposit a desired metal That is, the reaction of  $Mn^{++} + ne \rightarrow M$  occurs in cathode. At this time, it is at the usual electroplating.  $2H^{++} + 2e \rightarrow H_2$  A reaction occurs in coincidence and hydrogen occurs. Next, nonelectrolytic plating is explained. Generally the approach of chemistry reduction is used with nonelectrolytic plating. This principle is in depositing a metal ion chemically from metal salting in liquid using the chemical used as a reducing agent. For example, in the non-electrolytic copper plating which used formalin as a reducing agent, in plating liquid, it is  $Cu^{2++} + HCHO + 3OH \rightarrow HCOO + 2H_2O + Cu$ . A reaction occurs and Cu deposits on the galvanized

body. Moreover, it is  $\text{HCHO} + \text{OH}^- \rightarrow \text{HCOO}^- + \text{H}_2$  at this time. A reaction occurs in coincidence and hydrogen occurs. Although emitted also into atmospheric air, as for the hydrogen generated by detailed investigation of this invention person at the time of said plating, it turned out that remarkable hydrogen is incorporated also in the plating film.

[0004]

[Problem(s) to be Solved by the Invention] this invention person investigated wholeheartedly the cause in which the R-T-B system permanent magnet which covered plating carries out heat demagnetization greatly. Consequently, it discovered that heat demagnetization of a R-T-B system permanent magnet changed a lot depending on the amount of content hydrogen under plating. It has turned out that the problem to which a plating part is heated where hydrogen was held during plating at 100 ppm super-**\*\* rare \*\*\*\*\*** and is held like the rotating machine of an automobile etc. in a conventional R-T-B system permanent magnet in a high temperature environment at a sake, although the detailed mechanism was not clear, hydrogen gas is notably generated, and heat demagnetization of a R-T-B system permanent magnet object becomes large with regards to this hydrogen generated notably is generated. Therefore, by reducing the amount of hydrogen contained in the plating in the galvanized R-T-B system permanent magnet to 100 ppm or less, the technical problem of this invention is offering the R-T-B system permanent magnet which improved the thermal resistance of magnetic properties while it is excellent in corrosion resistance.

[0005]

[Means for Solving the Problem] this invention person studied wholeheartedly the cause by which the thermal resistance of the magnetic properties of the R-T-B system permanent magnet which covered plating deteriorated greatly. Consequently, the hydrogen contained in plating was emitted at the time of heating, and it discovered that the emitted hydrogen is absorbed by the R-T-B system permanent magnet object and that correlation was between heat-resistant degradation of the magnetic properties. This invention which solved the above-mentioned technical problem is the R-T-B system permanent magnet which came to cover plating to the R-T-system permanent magnet body surface which makes the main phase an R2T14B mold intermetallic compound (R is one sort of the rare earth elements containing Y, or two sorts or more, and T is Fe, or Fe and Co), and reduced the hydrogen content of said plating to 100 ppm or less.

[0006] Although plating pretreatment (pickling) is usually performed before plating, the conditions of this plating pretreatment are not limited and can adopt well-known conditions. For example, a nitric acid, hydrochloric acids, or those mixed acids may perform pickling. Or electrolytic cleaning, cleaning processing, etc. may be performed if needed. Moreover, activation may be performed when performing nonelectrolytic plating. Although the metal (alloy) to galvanize and the conditions of plating are not limited, the electrical and electric equipment and/or nonelectrolytic plating which consist of one monolayer coats of nickel, nickel-P, and Cu, Zn, Cr and Sn or two or more sorts of these multilayer coats are desirable practically. Furthermore, the resin paint or chromate treatment (+ alkali treatment) by electrodeposition may be performed on said plating layer if needed, and the corrosion resistance and good adhesive property which improved further can be realized. For example, electrical potential differences are [ 0.5-5V, and cathode current density ] 0.01 - 1.0 A/dm<sup>2</sup>, and electrical potential differences are [ 1-3V, and the cathode current density of the suitable conditions with which a hydrogen content covers electric nickel plating 100 ppm or less ] 0.05 - 0.5 A/dm<sup>2</sup> more preferably. Although for 30 - 240 minutes is practical as for the processing time of nickel plating, it is good to extend suitably according to desired nickel plating thickness. If nickel plating is performed by 5V super-**\*\*\*\*\* 1.0 A/dm<sup>2</sup> \*\***, cathode efficiency falls, the charge which is not used for electrodeposition of nickel will be emitted as hydrogen, and the amount of hydrogen finally incorporated by nickel plating will degrade greatly the thermal resistance of 100 ppm super-next door magnetic properties. The problem on which nickel plating electrodeposited while the electrodeposited effectiveness of nickel plating fell notably, when less than said nickel plating conditions exfoliates is generated. According to said electric nickel plating conditions, 3-50-micrometer nickel plating can usually be covered with average thickness. Moreover, specified quantity addition of brighteners, such as saccharin, a butynediol, or thiourea, and the **\*\*\*\*\*** may be carried out into plating liquid. It is desirable to carry out 0.1-0.5 g/dm<sup>3</sup> (g/l.) content of the sodium lauryl sulfate which is one sort of a surfactant into plating liquid especially. The content in

the plating liquid of sodium lauryl sulfate is not accepted for the addition effectiveness by less than three 0.1 g/dm, but, as for 0.5 g/dm<sup>3</sup> super-\*\*, the throwing power of electrolytic colouring of plating falls notably. A detailed examination of this invention person showed that correlation was between that the surface tension of specified quantity \*\*\*\* plating liquid declines notably, and the reduction effectiveness of the amount of hydrogen incorporated into the plating film about sodium lauryl sulfate.

[0007] When it constitutes the R-T-B system permanent magnet of this invention using the R-T-B system rare earth sintered magnet object which makes the main phase an R<sub>2</sub>T<sub>14</sub>B mold intermetallic compound, it is desirable to consider as Remainder T R:27 - 34% and B:0.5 to 2%, using the sum total of R of a major component, and B and T as 100 % of the weight. Hereafter, only describing it as % shows weight %. Furthermore, content of 0.6% or less of oxygen, 0.2% or less of carbon, 0.08% or less of nitrogen, 0.02% or less of hydrogen, and 0.2% or less of calcium is permitted as an unescapable impurity component, using AUW of said R-T-B system rare earth sintered magnet object as 100%. as R (Nd, Dy) -- or Dy or Pr -- or (Dy, Pr) -- or (Nd, Dy, Pr) it is chosen practically. 27 - 34% of the amount of R is desirable. If coercive force iH<sub>c</sub> declines greatly at less than 27% and the amount of R exceeds 34%, a residual magnetic flux density Br will fall greatly. 0.5 - 2% of the amount of B is desirable, and is more desirable. [ 0.8 - 1.5% of ] iH<sub>c</sub> to which the amount of B is equal to practical use at less than 0.5% is not obtained, but Br falls greatly by \*\* 2%. In order to improve magnetic properties, it is desirable to carry out optimum dose content of one sort of Nb, aluminum, Co, Ga, and Cu or the two sorts or more. The content of Nb is made into 0.1 - 2%. The way ghost of Nb generates in a sintering process by addition of Nb, and abnormality grain growth of crystal grain is controlled. Nb content is not accepted for the addition effectiveness at less than 0.1%, but in \*\*, the amount of generation of the way ghost of Nb increases 2%, and Br falls greatly. The content of aluminum is made into 0.02 - 2%. aluminum content is not accepted for the addition effectiveness at less than 0.02%, but Br falls rapidly by \*\* 2%. Co content is made into 0.3 - 5%. At less than 0.3%, the Curie point and the improvement effectiveness of adhesion with nickel plating are not practically acquired for Co content, but Br and iH<sub>c</sub> fall by \*\* 5%. Ga content is made into 0.01 - 0.5%. Ga content is not accepted for the improvement effectiveness of iH<sub>c</sub> at less than 0.01%, but the fall of Br becomes remarkable by \*\* 0.5%. Cu content is made into 0.01 - 1%. Although minute amount addition of Cu brings about iH<sub>c</sub> and corrosion resistance improvement, if Cu content exceeds 1%, the addition effectiveness will be saturated and the addition effectiveness will not be accepted at less than 0.01%.

[0008]

[Embodiment of the Invention] Hereafter, this invention is not limited by these examples although an example explains this invention to a detail.

(Example 1) 30%Nd-68.9%Fe-1.1%B The sintered magnet object which has a major component presentation was processed into rectangular plate-like [ with a 3mm/ 5mm by / x thickness of 0.7mm ]. Next, this processed magnet object was rinsed after immersion for 2 minutes in the aqueous acids of nitric-acid 2vol.%. Then, nickel plating was performed for 120 minutes by current density:0.1 A/dm<sup>2</sup> and electrical-potential-difference:3V after supplying the specified quantity of the rinsed magnet object to a barrel. the presentation of a plating bath -- nickel-sulfate: -- 240 g/dm<sup>3</sup> (g/l.), nickel chloride:40 g/dm<sup>3</sup> (g/l.), and boric-acid:30 g/dm<sup>3</sup> (g/l.) it is -- bath temperature could be 50 degrees C. Rinsing and desiccation were performed after nickel plating, and the R-T-B system permanent magnet of this invention which covered nickel plating of 10 micrometers of average thickness was obtained. Next, nickel plating film of said permanent magnet is stripped off, and it was failed to delete a part for an adhering magnet soma. Then, the amount of hydrogen contained in this nickel plating film was measured by the gas-chromatography method. A result is shown in Table 1. Next, 30 permanent magnets (P<sub>c</sub>=0.42) of said this invention were prepared. Next, in the room temperature, the amount phi 1 of total magnetic flux was measured after magnetization on the conditions with which the amount of total magnetic flux is saturated in each. Then, the ON furnace was carried out in atmospheric air and into the 70-degree C thermostat, ten pieces were taken out after 1-hour maintenance, and it returned to the room temperature. Moreover, the ten of 20 pieces remaining were taken out after 24-hour maintenance, and they were returned to the room temperature. Moreover, the ten remaining pieces were taken out after 48-hour maintenance, and were

returned to the room temperature. And each amount phi 2 of total magnetic flux of these 30 pieces was calculated for the percentage reduction of the amount of total magnetic flux by the following formula after measurement in the room temperature. A result is shown in Table 1. In addition, the result of Table 1 is the average of ten pieces, respectively.

Percentage reduction  $= (\phi_1 - \phi_2) / \phi_1 \times 100$  of the amount of total magnetic flux (%)

phi1: The amount phi 2 of total magnetic flux in the room temperature before a heat test: The amount of total magnetic flux in the room temperature after a heat test [0009] (Example 2) the presentation of a plating bath -- nickel-sulfate: -- 240 g/dm<sup>3</sup> (g/l.), nickel chloride: 40 g/dm<sup>3</sup> (g/l.), boric-acid: 30 g/dm<sup>3</sup> (g/l.), and sodium-lauryl-sulfate: 0.3 g/dm<sup>3</sup> (g/l.) \*\* -- the R-T-B system permanent magnet was produced like the example 1 except having carried out. The same evaluation as an example 1 was performed henceforth. A result is shown in Table 1.

(Example 1 of a comparison) the conditions of nickel plating -- current density: -- the R-T-B system permanent magnet of the example of a comparison was produced like the example 1 except having considered as for 30 minutes by 2 A/dm<sup>2</sup> and electrical-potential-difference: 7V. The same evaluation as an example 1 was performed henceforth. A result is shown in Table 1.

(Example 2 of a comparison) 30%Nd-68.9%Fe-1.1%B produced in the example 1 The same heat test as an example 1 was performed in the condition with the magnet object which processed into rectangular plate-like [ with a 3mm/ 5mm by / x thickness of 0.7mm ] the sintered magnet object which has a major component presentation, and it asked for the percentage reduction of the amount of total magnetic flux. A result is shown in Table 1.

[0010]

[Table 1]

	N   めっき膜の 含有水素量 (ppm)	総磁束量の減少率 (%)		
		1 時間 保持後	24 時間 保持後	48 時間 保持後
実施例 1	24	0	0. 2	0. 6
実施例 2	13	0	0. 1	0. 4
比較例 1	124	0. 9	4. 3	10. 3
比較例 2	—	0	0. 2	0. 5

[0011] The comparison with the examples 1 and 2 of Table 1 and the example 1 of a comparison shows that the percentage reduction of the amount of total magnetic flux becomes very small, when the amount of content hydrogen of nickel plating is 100 ppm or less. Moreover, it turns out that it has the percentage reduction of the low amount of total magnetic flux equivalent to the thing of the example 2 of a comparison with which the thing of the examples 1 and 2 which set the amount of content hydrogen of nickel plating to 100 ppm or less does not cover nickel plating from the comparison with the examples 1 and 2 of Table 1, and the example 2 of a comparison. Moreover, it turned out that the thing of the examples 1 and 2 after the above-mentioned heat test is presenting the good appearance, and it has the thing of the example 1 of a comparison, and the corrosion resistance more than an EQC. In order to set more preferably to 50 ppm or less 100 ppm or less of hydrogen contents which reduce the amount of hydrogen generated like the R-T-B system permanent magnet of examples 1 and 2 at the time of electric nickel plating, and are incorporated in the plating film, it is desirable to adopt the conditions which made current efficiency at the time of electroplating 98% or more more preferably 97% or more.

[0012] Although the above-mentioned example indicated the case where electric nickel plating of a monolayer was covered, this invention includes the case where it was not limited to this, for example, the three layer plating of nickel/nickel/nickel by electroplating and/or nonelectrolytic plating is covered. Moreover, the case where the three layer plating of nickel/Cu/nickel by electroplating and/or nonelectrolytic plating is covered, for example is included.

[0013] This invention includes what was not limited to a R-T-B system sintered magnet, made the main phase the R2T14B mold intermetallic compound, and covered plating on the R-T-B system warm working magnet object whose diameter of average crystal grain is 0.01-0.5 micrometers. Or what galvanized on the R-T-B system permanent magnet object which performed hot working to the casting alloy which adjusted the R2T14B mold intermetallic compound to the major component

presentation made into the main phase, and ingoted it, and gave the anisotropy to it is included.

[0014]

[Effect of the Invention] Above, according to this invention as description, while excelling in corrosion resistance, the galvanized R-T-B system permanent magnet with very little degradation of the magnetic properties at the time of heating can be offered.

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SOLUTION: The R-T-B permanent magnet whose surface is coated with the plating, where an R2T14B base intermetallic compound (R is one kind, or two kinds or more of rare earth elements which include Y, and T is Fe or Fe and Co) is a main phase, characterized in that the content of hydrogen of the plating is set equal to 100 ppm or lower.

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(54) 【発明の名称】 R-T-B系永久磁石

(57) 【要約】

【課題】 めっきしたR-T-B系永久磁石におけるめ  
つきに含有される水素量を100ppm以下に低減すること  
により、耐食性に優れるとともに磁気特性の耐熱性を向上  
したR-T-B系永久磁石を提供する。

【解決手段】 R、T、B型金属間化合物(RはYを  
含む希土類元素の1種または2種以上であり、TはFe  
またはFeとCoである)を主相とするR-T系永久  
磁石体表面にめっきを被覆してなるR-T-B系永久磁  
石であって、前記めっきの水素含有量を100ppm以下にし  
たことを特徴とするR-T-B系永久磁石。

## 【特許請求の範囲】

【請求項1】 R・T・B型金属間化合物（RはYを含む希土類元素の1種または2種以上であり、TはFeまたはFeとCoである）を主相とするR-T-B系永久磁石体表面にめっきを被覆してなるR-T-B系永久磁石であって、前記めっきの水素含有量を100ppm以下にしたことを特徴とするR-T-B系永久磁石。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は回転機（モータ、発電機）、アクチュエータ、スピーカまたはポンプ等に用いられる、めっきを被覆してなるR-T-B系永久磁石に関するものである。

## 【0002】

【従来の技術】希土類永久磁石のうち、R・T・B型金属間化合物を主相とするR-T-B系系焼結磁石（RはYを含む希土類元素の1種または2種以上であり、TはFeまたはFeとCoである）は高い磁気特性を有しており、フェライト磁石に次いでコストパフォーマンスに優れることから、近年製造量が大きく伸びている。しかしながら、その主要成分として希土類元素および鉄を多量に含有するために腐食しやすいという欠点を有しており、耐食性を向上するための種々の表面処理が施されて実用に供されている。表面処理膜として、樹脂コーティング、クロメート膜あるいはめっきなどが採用されているが、特にNiめっきに代表される金属皮膜をめっきする方法が耐食性および耐磨耗性等に優れており多用されている。めっきを被覆したR-T-B系永久磁石は各種磁石応用製品に組み込まれて使用されるが、近年耐熱仕様のニーズが増大してきている。めっきを被覆した従来のR-T-B系永久磁石は磁気特性の耐熱性が悪いという問題を有する。すなわち、従来のめっきしたR-T-B系永久磁石が未めっきのものに比べて加熱時の総磁束量の減少率が顕著に大きくなるという問題がある。例えば、後述するように、縦5mm×横3mm×厚み0.7mm程度の長方形板状のR-Fe-B系永久磁石体にNiめっきを被覆したもの（パーミアンス係数 $\mu_c=0.42$ ）を作製後、続いて大気中の70℃で所定時間保持後室温まで戻す加熱試験を行った場合、総磁束量の減少率は10%に達するほど大きい。このように、めっきした従来のR-T-B系永久磁石の加熱時の磁気特性の顕著な劣化は深刻な問題であった。

【0003】次に、めっきについて説明する。金属皮膜をめっきする方法は大きく電気めっきと無電解めっきとに分けられる。電気めっきでは、めっきしようとする金属イオンを含む電解液中で、被めっき体を陰極とし、電着させようとする金属と同じ金属かまたは不溶性の金属を陽極として、直流電解を行えば、陰極で電着させようとする金属イオンが放電し、被めっき体表面に所望の金

属を電着させることができる。つまり、陰極では $M^{n+} + ne \rightarrow M$ の反応が起こる。このとき、通常の電気めっきでは $2H^+ + 2e \rightarrow H_2$ の反応が同時に起こり、水素が発生する。次に無電解めっきについて説明する。無電解めっきで一般に用いられているのは化学還元法という方法である。この原理は、還元剤となる薬品を用いて、金属塩溶液から化学的に金属イオンを析出させることにある。例えばホルマリンを還元剤として用いた無電解銅めっきの場合、めっき液中では、 $Cu^{2+} + HCHO + 3OH^- \rightarrow HCOO^- + 2H_2O + Cu$ の反応が起こり、被めっき体にCuが析出する。また、このとき $HCHO + OH^- \rightarrow HCOO^- + H_2$ の反応が同時に起こり水素が発生する。本発明者の詳細な調査により、前記めっき時に発生した水素は大気中にも放出されるが、かなりの水素がめっき膜中にも取り込まれることがわかった。

## 【0004】

【発明が解決しようとする課題】本発明者はめっきを被覆したR-T-B系永久磁石が大きく熱減磁する原因を鋭意調査した。その結果、R-T-B系永久磁石の熱減磁がめっき中の含有水素量に依存して大きく変化することを発見した。詳細なメカニズムは明らかになっていないが、従来のR-T-B系永久磁石ではめっき中に水素が100ppm超含まれており、ために自動車の回転機等の如くの高温度環境に保持された状態ではめっき部分が加熱されて水素ガスが顕著に発生し、この顕著に発生した水素に関係してR-T-B系永久磁石体の熱減磁が大きくなる問題を発生することがわかってきた。したがって、本発明の課題は、めっきしたR-T-B系永久磁石におけるめっきに含有される水素量を100ppm以下に低減することにより、耐食性に優れるとともに磁気特性の耐熱性を向上したR-T-B系永久磁石を提供することである。

## 【0005】

【課題を解決するための手段】本発明者は、めっきを被覆したR-T-B系永久磁石の磁気特性の耐熱性が大きく劣化する原因を鋭意研究した。その結果、めっきに含まれる水素が加熱時に放出され、その放出された水素がR-T-B系永久磁石体に吸収されることと、その磁気特性の耐熱性の劣化との間に相関があることを発見した。上記課題を解決した本発明は、R・T・B型金属間化合物（RはYを含む希土類元素の1種または2種以上であり、TはFeまたはFeとCoである）を主相とするR-T-B系永久磁石体表面にめっきを被覆してなり、かつ前記めっきの水素含有量を100ppm以下に低減したR-T-B系永久磁石である。

【0006】めっきの前に通常めっき前処理（酸洗い）を行うが、このめっき前処理の条件は限定されるものではなく、公知の条件を採用することができる。例えば、硝酸、塩酸あるいはそれらの混合酸等で酸洗いを行ってもよい。あるいは必要に応じて電解洗浄、脱脂処理等を

行ってもよい。また、無電解めっきを行う場合は活性化処理を行ってもよい。めっきする金属（合金）およびめっきの条件は限定されるものではないが、実用上、Ni、Ni-P、Cu、Zn、Cr、Snのいずれかの単層皮膜あるいはこれらの2種以上の多層皮膜からなる、電気および／または無電解めっきが好ましい。さらに必要に応じて、前記めっき層の上に電着による樹脂塗装またはクロメート処理（+アルカリ処理）を施してもよく、さらに向上した耐食性および良好な接着性を実現できる。例えば水素含有量が100ppm以下の電気Niめっきを被覆する好適な条件は、電圧が0.5～5Vおよび陰極電流密度が0.01～1.0A/dm<sup>2</sup>であり、より好ましくは電圧が1～3Vおよび陰極電流密度が0.05～0.5A/dm<sup>2</sup>である。Niめっきの処理時間は30～240分間が実用的であるが、所望のNiめっき厚みに応じて適宜延長するのがよい。5V超および1.0A/dm<sup>2</sup>超でNiめっきを行うと、陰極電流効率が下がり、Niの電着に使われない電荷は水素として放出されて、最終的にNiめっきに取り込まれる水素量が100ppm超となり磁気特性の耐熱性を大きく劣化させる。前記Niめっき条件を下回るとNiめっきの電着効率が顕著に低下するとともに電着したNiめっきが剥離する問題を発生する。前記電気Niめっき条件によれば、通常平均膜厚で3～50μmのNiめっきを被覆できる。また、めっき液中にサッカリン、ブチンジオールまたはチオ尿素などの光沢剤、や界面活性剤を所定量添加してもよい。特に、界面活性剤の1種であるラウリル硫酸ナトリウムをめっき液中に0.1～0.5g/dm<sup>3</sup>（g/リットル）含有することが好ましい。ラウリル硫酸ナトリウムのめっき液中の含有量が0.1g/dm<sup>3</sup>未満では添加効果が認められず、0.5g/dm<sup>3</sup>超ではめっきのつきまわり性が顕著に低下する。本発明者の詳細な検討により、ラウリル硫酸ナトリウムを所定量含むめっき液の表面張力が顕著に低下することとめっき膜中へ取り込まれる水素量の低減効果との間に相関があることがわかった。

【0007】R、T、B型金属間化合物を主相とするR-T-B系希土類焼結磁石体を用いて本発明のR-T-B系永久磁石を構成する場合、主要成分のRとBとTとの合計を100重量%として、R：27～34%、B：0.5～2%、残部Tとすることが好ましい。以下、単に%と記しているのは重量%を示す。さらに、前記R-T-B系希土類焼結磁石体の総重量を100%として、不可避不純物成分として0.6%以下の酸素、0.2%以下の炭素、0.08%以下の窒素、0.02%以下の水素、0.2%以下のCaの含有が許容される。Rとして（Nd、Dy）またはDyまたはPrまたは（Dy、Pr）または（Nd、Dy、Pr）が実用上選択される。R量は27～34%が好ましい。R量が27%未満では保磁力iHcが大きく低下し、34%を超えると残留磁束密度Brが大きく低下する。B量は0.5～2%が好ましく、0.8～1.5%がより好ましい。B量が0.5%未満では実用に耐えるiHcが得られず、2%超で

はBrが大きく低下する。磁気特性を改善するために、Nb、Al、Co、Ga、Cuの1種または2種以上を適量含有することが好ましい。Nbの含有量は0.1～2%とされる。Nbの添加により焼結過程でNbのほう化物が生成し、結晶粒の異常粒成長を抑制する。Nb含有量が0.1%未満では添加効果が認められず、2%超ではNbのほう化物の生成量が多くなりBrが大きく低下する。Alの含有量は0.02～2%とされる。Al含有量が0.02%未満では添加効果が認められず、2%超ではBrが急激に低下する。Co含有量は0.3～5%とされる。Co含有量が0.3%未満ではキュリー点、Niめっきとの密着性の向上効果が実用上得られず、5%超ではBr、iHcが低下する。Ga含有量は0.01～0.5%とされる。Ga含有量が0.01%未満ではiHcの向上効果が認められず、0.5%超ではBrの低下が顕著になる。Cu含有量は0.01～1%とされる。Cuの微量添加はiHcおよび耐食性の向上をもたらすが、Cu含有量が1%を超えると添加効果は飽和し、0.01%未満では添加効果が認められない。

#### 【0008】

【発明の実施の形態】以下、実施例により本発明を詳細に説明するが、それら実施例により本発明が限定されるものではない。

（実施例1）30%Nd-68.9%Fe-1.1%Bの主要成分組成を有する焼結磁石体を、縦5mm×横3mm×厚み0.7mmの長方形板状に加工した。次に、この加工した磁石体を硝酸2vol.%の酸性水溶液中に2分間浸漬後水洗した。続いて、水洗した磁石体の所定量をバレルに投入後、電流密度：0.1A/dm<sup>2</sup>、電圧：3Vで120分間Niめっきを行った。めっき浴の組成は硫酸ニッケル：240g/dm<sup>3</sup>（g/リットル）、塩化ニッケル：40g/dm<sup>3</sup>（g/リットル）、ホウ酸：30g/dm<sup>3</sup>（g/リットル）であり、浴温は50℃とした。Niめっき後、水洗および乾燥を行い、平均膜厚10μmのNiめっきを被覆した本発明のR-T-B系永久磁石を得た。次に、前記永久磁石のNiめっき膜を剥ぎ取り、付着している磁石体部分を削り落とした。続いて、このNiめっき膜中に含まれる水素量をガスクロマトグラフィー法により測定した。結果を表1に示す。次に、前記本発明の永久磁石（Pc=0.42）を30個準備した。次に、室温において、各々を総磁束量が飽和する条件で着磁後、総磁束量Φ1を測定した。続いて、大気中、70℃の恒温槽内に入炉して1時間保持後10個を取り出し、室温に戻した。また、残りの20個のうち10個は24時間保持後に取り出し、室温に戻した。また、残りの10個は48時間保持後に取り出し、室温に戻した。そして、それら30個の各々の総磁束量Φ2を室温において測定後、下記式により総磁束量の減少率を求めた。結果を表1に示す。なお、表1の結果はそれぞれ10個の平均値である。

総磁束量の減少率＝(Φ1－Φ2)／Φ1×100(%)  
Φ1：加熱試験前の室温における総磁束量

Φ2：加熱試験後の室温における総磁束量

【0009】（実施例2）めっき浴の組成を硫酸ニッケル：240 g/dm<sup>3</sup>（g/リットル）、塩化ニッケル：40 g/dm<sup>3</sup>（g/リットル）、ホウ酸：30 g/dm<sup>3</sup>（g/リットル）、ラウリル硫酸ナトリウム：0.3 g/dm<sup>3</sup>（g/リットル）とした以外は実施例1と同様にしてR-T-B系永久磁石を作製した。以降は実施例1と同様の評価を行った。結果を表1に示す。

（比較例1）Niめっきの条件を電流密度：2 A/dm<sup>2</sup>、電圧：7Vで30分間とした以外は実施例1と同様にして \* 10

\* 比較例のR-T-B系永久磁石を作製した。以降は実施例1と同様の評価を行った。結果を表1に示す。

（比較例2）実施例1で作製した、30%Nd-68.9%Fe-1.1%Bの主要成分組成を有する焼結磁石体を縦5mm×横3mm×厚み0.7mmの長方形板状に加工した磁石体のままの状態で行った実施例1と同様の加熱試験を行い、総磁束量の減少率を求めた。結果を表1に示す。

【0010】

【表1】

	Niめっき膜の 含有水素量 (ppm)	総磁束量の減少率 (%)		
		1時間 保持後	24時間 保持後	48時間 保持後
実施例1	24	0	0.2	0.6
実施例2	13	0	0.1	0.4
比較例1	124	0.9	4.3	10.3
比較例2	—	0	0.2	0.5

【0011】表1の実施例1、2と比較例1との比較から、Niめっきの含有水素量が100ppm以下のときに総磁束量の減少率が非常に小さくなるのがわかる。また、表1の実施例1、2と比較例2との比較から、Niめっきの含有水素量を100ppm以下とした実施例1、2のものがNiめっきを被覆しない比較例2のものと同等の低い総磁束量の減少率を有することがわかる。また、上記加熱試験後の実施例1、2のものは良好な外観を呈しており、比較例1のものと同等以上の耐食性を有することがわかった。実施例1、2のR-T-B系永久磁石の如く、電気Niめっき時に発生する水素量を低減してめっき膜中に取り込まれる水素含有量を100ppm以下、より好ましくは50ppm以下にするために、電気めっき時の電流効率を97%以上、より好ましくは98%以上にした条件を採用することが望ましい。

【0012】上記実施例では、単層の電気Niめっきを被覆した場合を記載したが、本発明はこれに限定されず、例えば電気めっきおよび/または無電解めっきによ

※るNi/Ni/Ni3層めっきを被覆した場合を包含する。また、例えば電気めっきおよび/または無電解めっきによるNi/Cu/Ni3層めっきを被覆した場合を包含する。

【0013】本発明はR-T-B系焼結磁石に限定されず、R-T-B型金属間化合物を主相とし、かつ平均結晶粒径が0.01~0.5μmであるR-T-B系温間加工磁石体にめっきを被覆したものを包含する。あるいはR-T-B型金属間化合物を主相とする主要成分組成に調整して溶製した鋳造合金に熱間加工を施して異方性を付与したR-T-B系永久磁石体にめっきを施したものを包含する。

【0014】

【発明の効果】上記記述の通り、本発明によれば、耐食性に優れるとともに加熱時の磁気特性の劣化が非常に少ないめっきしたR-T-B系永久磁石を提供することができる。

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